lactone 3 and the dithiolactone 12, it was dissolved in methanolic sodium methoxide, cooled, diluted with water, and acidified. The crude 5 thus obtained was dissolved in 5% sodium carbonate, the insoluble fraction was removed by filtration, and the solution was extracted with ether. Acidification gave pure 5, which was dissolved in 50 ml of methanol and refluxed for 35 min to give 1.5 g of 7 as long yellow needles: mp 175-176.5°; ir (Nujol) 5.6, 5.9, 6.2 μ; nmr ($CDCl_3$) δ 7.30 (m, 6, phenyl H), 7.80 (m, 4, phenyl H); mass spectrum *m/e* 306 (M^+), 278, 250.

Anal. Calcd for $C_{18}H_{10}O_3S$: C, 70.57; H, 3.29; S, 10.47. Found: C, 70.89; H, 3.41; S, 10.23.

5-Carbomethoxy-2,5-diphenyl-3-hydroxy-4-mercapto-2,4-pentadienoic Acid γ-Thiolactone (*E*) (5). A solution of 1.6 g (0.00523 mol) of 7 and 1.6 g (0.03 mol) of sodium methoxide in 35 ml of methanol was kept at 0-5° for 30 min. The solution was treated with charcoal and diluted with water, and the chilled solution was acidified with HCl to give a yellow solid. This was dissolved in about 200 ml of 5% Na_2CO_3 and extracted twice with ether, and the aqueous layer was acidified in the cold with acetic acid to give 1.50 g (84%) of a yellow-orange, flocculent solid: mp 115-116° (resolidified and remelted at 173-175°); ir (Nujol) broad peak at 3.9-4.4 (chelated OH), 5.94 and 6.03 μ; nmr ($CDCl_3$) δ 3.76 (s, 3, OCH_3), 7.31 (m, 8, phenyl H), 7.72 (m, 2, phenyl H), 13.97 (br s, 1, OH); mass spectrum *m/e* 338 (M^+), 306 ($M^+ - CH_3OH$), 278.

Anal. Calcd for $C_{19}H_{14}O_4S$: C, 67.44; H, 4.17; S, 9.48. Found: C, 67.74; H, 4.29; S, 9.19.

3,6-Diphenyl-2*H*,5*H*-thieno[3,2-*b*]thiophene-2,5-dione (12). A mixture of 5.0 g (0.0172 mol) of pulvinic acid lactone, 4 ml of thiolacetic acid, 8 ml of chloroform, and 22 ml of dry pyridine was refluxed for 3 hr. Then another 4 ml of thiolacetic acid was added, the refluxing was continued for an additional 1 hr, and the reaction mixture was allowed to stand at room temperature for 18 hr. This gave 0.90 g (16%) of an orange solid, mp 219-221.5°. For purification this was dissolved in warm methanolic sodium methoxide to give a red solution. The chilled solution was diluted with water and acidified to give a yellow solid, which was slurried with sodium carbonate and washed with water to give 0.65 of a yellow solid: mp 221-222.5° dec; ir 5.9 μ; mass spectrum *m/e* 322 (M^+).

Anal. Calcd for $C_{18}H_{10}O_2S_2$: C, 67.06; H, 3.13; S, 19.89. Found: C, 67.08; H, 3.32; S, 19.55.

Acknowledgments. We are indebted to our Analytical and Physical Chemistry Section personnel for analytical and physical data: Miss Edith Reich for elemental analysis and Dr. Edward White and Mr. Gerald Roberts for mass spectra.

Registry No.—**2**, 51751-95-2; **3**, 6273-79-6; **4**, 51751-96-3; **5**, 51751-97-4; **7**, 51751-98-5; **10**, 51751-99-6; **11**, 51751-00-2; **12**, 51751-01-3.

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An Improved Synthesis of Tetrathiafulvalene

L. Russell Melby,* Harris D. Hartzler, and William A. Sheppard

Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898[1]

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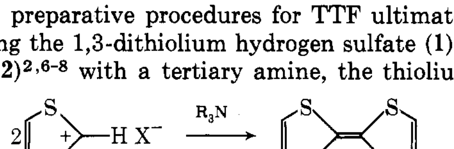
The phenomenon of metallic electrical conductivity in the complex of tetrathiafulvalene (TTF, 3) with tetracyanoquinodimethane has recently been a subject of intense interest.[2-4] Extensive physical study of this complex depends, among other things, upon a reliable source of TTF, which must be unusually pure.[5] In our hands existing routes to TTF proved to be tedious and difficult to reproduce, and often gave product of dubious or unsatisfactory purity. We now report an improved synthesis of TTF.

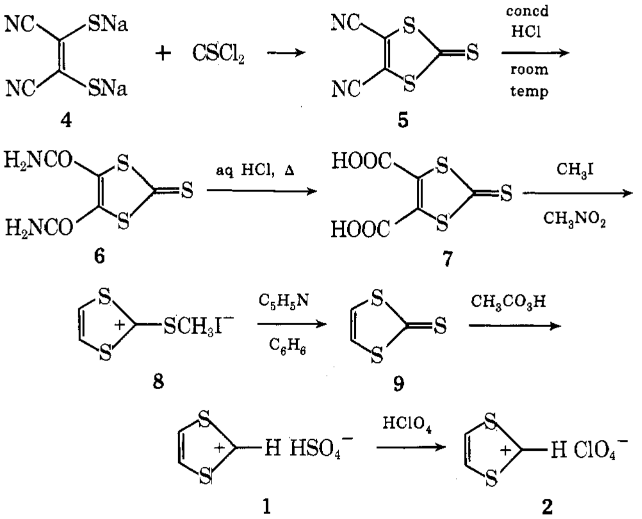
Typical preparative procedures for TTF ultimately rely on coupling the 1,3-dithiolium hydrogen sulfate (1) or perchlorate (2)[2,6-8] with a tertiary amine, the thiolium salts



1, X = HSO_4^-
2, X = ClO_4^-

3

being obtained by the method of Klingsberg.[9] The latter entails the multistep sequence depicted in transformations 4 through 9.



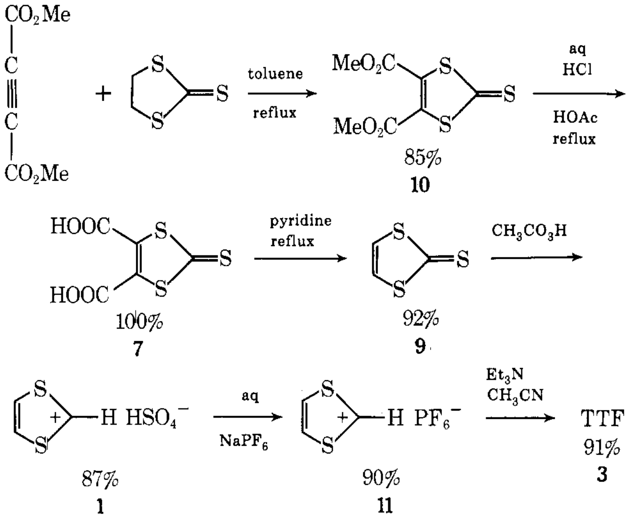
In this sequence we encountered particular difficulty in obtaining reasonable yields of thione 9 by demethylation of the methiodide 8. This in turn complicated preparing pure hydrogen sulfate 1. Furthermore, although the hydrogen sulfate can be directly coupled to TTF without conversion to an intervening salt form, the fact that it is hygroscopic and difficult to purify seriously compromises its use as a coupling substrate. The hydrogen sulfate can be readily converted to very pure perchlorate 2, which is chemically satisfactory for coupling, but which entails a serious explosion hazard particularly if large quantities are to be used.

Our improved procedure begins with the diester 10 prepared according to the directions of O'Connor and Jones.[10]

By this means we have reproducibly obtained recrystallized TTF of very high purity in 65% yields based on diester 10, or 55% overall yields based on commercially available dimethyl acetylenedicarboxylate and ethylene trithiocarbonate; the yields cited are reproducible to within ±2%.

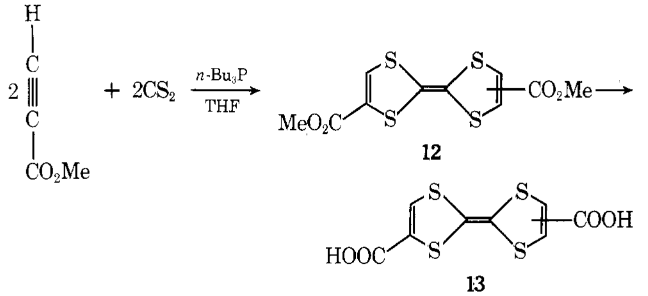
In addition to high yields, the main points of advantage and novelty in this sequence are (1) a simplified route to diacid 7, (2) direct decarboxylation of the diacid to thione 9 in high yield and purity and consequent improved accessibility of the hydrogen sulfate 1, (3) formation of analytically pure PF_6^- salt 11, which is an ideal coupling substrate both with respect to the chemistry of coupling and safety of handling even on a large scale.[11]

For spectral studies we also required highly deuterated TTF. By hydrolyzing the ester 10 with a mixture of DCl and DOAc in D_2O (from acetyl chloride and D_2O), and

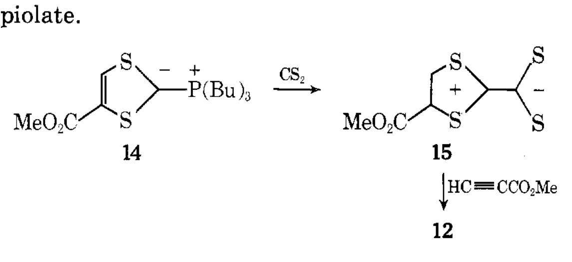


continuing the series as above, we obtained TTF deuterated to the extent of 96% and in 64% yield based on the diester.

In examining other routes to TTF it was found that 4,4′(5′)-bis(carbomethoxy)-$\Delta^{2,2'}$-bi-1,3-dithiole (12) was formed in modest yield by the reaction of methyl propiolate, tributylphosphine, and carbon disulfide in tetrahydrofuran (THF) at −30°. Alkaline hydrolysis of the diester and decarboxylation of the resulting diacid (13) afforded TTF in 13% overall yield based on methyl propiolate.



The formation of the diester 12 is somewhat difficult to rationalize, but is presumably mediated by the phosphorane 14;[12] if the latter were a sufficiently potent nucleophile it could attack carbon disulfide to form an intermediate of type 15 which could further react with methyl propiolate.



Experimental Section

Dimethyl 1,3-Dithiole-2-thione-4,5-dicarboxylate (10).[10] The reaction of dimethyl acetylenedicarboxylate with ethylene trithiocarbonate in refluxing toluene was conducted on a 5-mol scale. After refluxing for a minimum of 6 hr the solution was chilled and the first crop was collected, yield 742 g (59%), mp 86–87° (lit.[10] mp 72–72.5). Successive concentration of the liquors gave additional crops of material which was less pure, but adequate for subsequent hydrolysis. Combined total yields amounted to 80–85%, nmr (DMSO-d_6) δ 3.83.

1,3-Dithiole-2-thione-4,5-dicarboxylic Acid (7). A mixture of 100 g (0.4 mol) of the diester 10, 600 ml of water, 430 ml of concentrated hydrochloric acid, and 200 ml of glacial acetic acid was boiled under reflux for 2 hr and then chilled in an ice bath. The solid was collected without washing, sucked dry under a stream of nitrogen, and dried in a vacuum desiccator over phosphorus pentoxide and potassium hydroxide, yield 72 g (81%), mp 165–167° dec (lit.[9] mp *ca.* 160° dec). The mothor liquor was evaporated to dryness to obtain a second crop, 17 g, mp 164–167°. The combined total yield was quantitative, nmr (DMSO-d_6) δ 15.48.

1,3-Dithiole-2-thione (9). A mixture of 22.2 g (0.1 mol) of the diacid 7 in 100 ml of pyridine was boiled under reflux for 3 hr. The mixture was concentrated to a thick black oil on a vacuum rotary evaporator with gentle heating (40–50°) until the thione began to show as a thin yellow film in the neck of the flask. To the oil was added 500 ml of hexane which was refluxed under nitrogen for 0.5 hr. The hot hexane was decanted into a flask and chilled in a Dry Ice-acetone mixture to obtain the thione as long, yellow, silky needles. The residual oil was subjected to four such extractions to obtain a total of 12.3 g of thione (93% yield), mp 48–49° (lit.[9] mp 50–51°), nmr ($CDCl_3$) δ 7.17.

1,3-Dithiolium Hydrogen Sulfate (1). A solution of 12.7 g (0.095 mol) of thione 9 in 250 ml of acetone was cooled to −50° in a Dry Ice–acetone bath and a solution of 73 g (0.38 mol) of 40% peracetic acid and 150 ml of acetone was added dropwise, with stirring at such a rate that the temperature did not rise above −40° (about 15 min). The cooling bath was removed and, with continued stirring, the mixture was allowed to warm spontaneously. Within 15–20 min the reaction became rapidly exothermic and when the temperature had risen to 15° the cooling bath was immediately replaced. When the temperature had again reached −50° the bath was removed and the mixture was again allowed to warm spontaneously. No further exotherm occurred and when the temperature reached 5–10° the solid was collected, washed with 100 ml of cold acetone, and sucked dry under a nitrogen stream, yield 16.6 g (87%), mp 123–125° dec (lit.[9] mp *ca.* 125° dec).

1,3-Dithiolium Hexafluorophosphate (11). In 200 ml of deaerated water was dissolved 42 g (0.21 mol) of the hydrogen sulfate 1, Darco was added, and the soluton was filtered through a Celite pad directly into a previously filtered solution of 38 g (0.23 mol) of sodium hexafluorophosphate in 100 ml of water. The flask was flushed with nitrogen, capped, swirled gently, and refrigerated at 5–10° for 4 hr. The white solid was collected, washed with 50 ml of cold water, and sucked dry under a stream of nitrogen, yield 46 g (90%), mp *ca.* 150–200° dec. *Anal.* Calcd for $C_3H_3S_2PF_6$ (248.17): C, 14.5; H, 1.2; S, 25.8. Found: C, 14.8; H, 1.5; S, 25.9.

Tetrathiafulvalene (3). A solution of 45 g (0.18 mol) of the thiolium hexafluorophosphate (11) in 800 ml of anhydrous acetonitrile was filtered through a medium-frit funnel directly into a 5-l. flask equipped with a nitrogen inlet, dropping funnel, and magnetic stirrer. After purging with nitrogen for 15 min, 28 ml (0.2 mol) of triethylamine was added dropwise during about 15 min with stirring at room temperature.[13] Stirring was continued for 15 min more and then 3 l. of deaerated water was added to precipitate the TTF as a flocculent, dull orange solid. After 10 min of stirring the solid was collected, washed with water, and sucked dry under a stream of nitrogen. The crude yield was 18.2 g (98%), mp 118–119° (lit.[6] mp 120°). The crude product was dissolved in 1 l. of boiling cyclohexane, treated with Darco, filtered hot, and immediately diluted with 400 ml of *n*-hexane. After cooling overnight at 5–10° the product crystallized as long, orange needles, yield 14.7 g (81% recovery), mp 119–119.5°. The mothor liquor was evaporated under a nitrogen stream to a volume of 150 ml, and the mixture was reheated to dissolve the solid and chilled as before to obtain a second crop, yield 2.1 g, mp 119–119.5°. The total yield was thus 16.8 g (91%), nmr ($CDCl_3$) δ 6.32, ir (Nujol) 1530, 1250, 1090, 795, 780, and 730 cm^{-1}.

Tetrathiafulvalene-d_4. A hydrolysis medium was prepared by carefully adding 100 ml of redistilled acetyl chloride to 280 ml of D_2O contained in a flask with a Dry Ice condenser. Beginning with this mixture and 30 g of diester 10 and carrying each intermediate through the above sequence appropriately scaled, there was obtained 8.0 g (64%) of recrystallized product, mp 119–119.5°. *Anal.* Calcd for $C_6D_4S_4$: C, 34.6; S, 61.6. Found: C, 34.6; S, 61.5.

Mass spectral analysis showed 0% d_0, 0% d_1, 1% d_2, 13% d_3, and 86% d_4 species corresponding to 96% deuterium exchange; ir (Nujol) 2290, 1500, 1160, 1040, 780, and 700 cm^{-1}.

Ordinary reagents were used throughout except for the hexafluorophosphate metathesis, where D_2O was used as the solvent.

4,4′(5′)-Bis(carbomethoxy)-$\Delta^{2,2'}$-bi-1,3-dithiole (12). Tributylphosphine (20.2 g, 0.1 mol) was added dropwise to a solution of 10 ml of carbon disulfide in 50 ml of tetrahydrofuran under nitrogen. The deep maroon solution was cooled to −30° and a solution of 8.4 g (0.1 mol) of methyl propiolate in 50 ml of tetrahydrofuran was added dropwise. The temperature was maintained between −20 and −30° during addition. The system was warmed to room temperature and volatiles were removed through the rotary evaporator. The residue was stirred with a little ether and filtered to give 3.3 g (21%) of the red, crystalline product which melted at 238–240°. Recrystallization from glyme gave material which melted at 244–245°: ir (Nujol) 3080 (w), 2950 (w), 1720 (s), 1550 (s), 1440 (m), 1250 (s), 1200 (m), 1160 (m), 1050 (m), 940 (m), 830 (m), 820 (m), 765 (m), 730 cm^{-1} (m); uv (CH_2Cl_2) λ 444 nm (ε 2470), 315 (11,000), 302 (10,600) and 290 (sh, 10,000).

Anal. Calcd for $C_{10}H_8O_4S_4$: C, 37.48; H, 2.52; S, 40.03. Found: C, 37.28; H, 2.54; S, 39.88.

$\Delta^{2,2'}$-Bi-1,3-dithiole-4,4′(5′)-dicarboxylic Acid (13). A heterogeneous system consisting of 3.2 g (0.01 mol) of the diester, 25 ml of 1 *N* sodium hydroxide, and 100 ml of tetrahydrofuran was heated at reflux for 45 min. The mixture was then homogeneous. It was acidified with 1 *N* hydrochloric acid and filtered to give 2.6 g (89%) of the red, crystalline acid. The acid did not melt under 350°: uv (0.01 *N* NaOH) λ_{max} 407 nm (ε 2570), 313 (13,000), 302 (12,600), 285 (sh); ir (Nujol) 3100–2500 (w), 1660 (s), 1540 (s), 1420 (s), 1290 (s), 1195 (m), 1040 (m), 840 (m), 825 (w), 775 (w), and 730 cm^{-1} (w).

Anal. Calcd for $C_8H_4O_4S_4$: C, 32.9; H, 1.4; S, 43.9. Found: C, 33.0; H, 1.6; S, 43.7.

Tetrathiafulvalene.[14] A mixture of 292 mg of the diacid and 10 ml of pyridine was sealed in a heavy-walled glass tube under vacuum after flushing with argon while freeze–thawing. The tube was heated at 240° for 1.5 hr. The tube was cooled and opened and the solvent was evaporated. The dark residue was extracted twice with 10-ml portions of acetonitrile. The extracts were evaporated and the residue was sublimed at 105° (0.1 Torr) to give 140 mg (69%) of the orange product. The sublimate melted at 114–116°.

Acknowledgment. We are indebted to Eleanor G. Applegate for expert technical assistance.

Registry No.—**1,** 51751-15-6; **3,** 31366-25-3; **3**-d_4, 51751-16-7; **7,** 1008-62-4; **9,** 930-35-8; **10,** 7396-41-0; **11,** 51751-17-8; **12,** 51751-18-9; **13,** 51751-19-0; dimethyl acetylenedicarboxylate, 762-42-5; ethylene trithiocarbonate, 822-38-8; tributylphosphine, 998-40-3.

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(13) When reaction is complete the mixture abruptly changes color from greenish-black to deep amber. If this change is not observed, additional drops of amine are added until it occurs.

(14) We are indebted to Dr. W. R. Hertler for this experiment.

Synthesis of Optically Active Sulfoximines from Optically Active Sulfoxides[1]

Carl R. Johnson,* Robert A. Kirchhoff, and H. Glenn Corkins

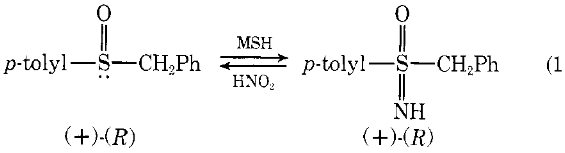
Department of Chemistry, Wayne State University, Detroit, Michigan 48202

Received February 15, 1974

Optically active sulfoximines are useful synthetic intermediates.[2] There are, however, only a few methods available for their preparation. One, involving resolution with (+)-10-camphorsulfonic acid, has been found useful only in the case of *S*-phenyl-*S*-methylsulfoximine.[3a,b] A resolution has been achieved by separation of *N*-(+)-10-camphorsulfonylsulfoximine diastereomers followed by removal of the resolving group by acid hydrolysis.[3c] The reaction of an optically active sulfoxide with tosyl azide in the presence of copper catalyst[4] results in optically pure *N*-tosylsulfoximines.[3b] Hydrolysis with strong acid is required to remove the *N*-tosyl group; the hydrolysis often fails and/or results in extensive decomposition. The direct preparation of optically active "free" sulfoximines using the hydrazoic acid method[5] is not applicable, since racemization of the starting sulfoxide occurs.[3b] This note describes a simple one-step method for the production of optically active sulfoximines in good yield and high enantiomeric purity.

Reaction of *O*-mesitylsulfonylhydroxylamine (MSH) with sulfides and sulfoxides has been reported to produce sulfilimines and sulfoximines, respectively.[6] In exploring the scope of this sulfoximine preparation we have found that the reaction of optically active sulfoxides with MSH results in sulfoximines of high optical purity. Table I shows the various optically active "free" sulfoximines prepared. By the nature of the various sulfoxides shown here and earlier[6] it can be seen that the imidation reaction is quite general.

When 99% pure (+)-(*R*)-methyl *p*-tolyl sulfoxide was treated with MSH, (−)-(*R*)-*S*-methyl-*S*-*p*-tolylsulfoximine was obtained in 98.5% optical purity. Likewise, (−)-(*S*)-methyl phenyl sulfoxide with 94% optical purity was converted to (+)-(*S*)-*S*-methyl-*S*-phenylsulfoximine of 93.5% purity. Since the absolute configurations of these sulfoximines are known[7,8] as well as the absolute configuration of the starting sulfoxides,[9,10] it can be stated that these reactions occur with retention of configuration at the sulfur atom. Deimidation of (+)-benzyl-*p*-tolyl sulfoximine with nitrous acid (eq 1) resulted in (+)-benzyl *p*-tolyl sulfoxide, which is known to have the *R* configuration.[9] Cram and coworkers have shown this reaction to occur with retention of configuration.[11]



$$\underset{(+)\text{-}(R)}{p\text{-tolyl}-\overset{\overset{\displaystyle O}{\|}}{\underset{\cdot\cdot}{S}}-CH_2Ph} \underset{HNO_2}{\overset{MSH}{\rightleftarrows}} \underset{(+)\text{-}(R)}{p\text{-tolyl}-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle NH}{\|}}{S}}-CH_2Ph} \qquad (1)$$

Experimental Section

Optical rotations were measured on a Perkin-Elmer 141 polarimeter using a 1-dm cell.

The alkyl aryl and diaryl sulfoxides were obtained by the Anderson method in which the corresponding Grignard reagent was treated with (−)-menthyl *p*-toluenesulfinate;[12] for information concerning the assignment of their absolute configuration see ref 9. The preparation of (−)-(*R*)-methyl *n*-butyl sulfoxide as well as its configurational assignment has been described.[13]

***O*-Mesitylsulfonylhydroxylamine (MSH).**[14] Ethyl *O*-(mesitylsulfonyl)acetohydroxamate (7.5 g) was dissolved in dioxane (5 ml) and cooled to 0° with stirring. To this was added 70% perchloric acid (3 ml) dropwise at a rate so as to maintain the temperature below 10°. The resulting mixture was added to ice water (300 ml), the crude MSH was filtered off, washed well with water, and dissolved in ether (30 ml). The ether solution wash washed with water (25 ml), treated with anhydrous potassium carbonate (5 g) for 30 sec and filtered. The ether solution was poured into cold pentane (300 ml) to precipitate the MSH as small crystals which were collected and dried under vacuum for 5 min at room temperature. Caution, this material may explode;[15] it should be stored in a plastic container sealed with plastic or wax film.

Optically Active Sulfoximines. Compounds **1a–h** were prepared by treating the corresponding optically active sulfoxide (2